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## VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.ON THE BEHAVIOR OF CERTAIN DERIVATIVES OF  
BENZOL CONTAINING HALOGENS.

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Presented May 9, 1894.

## INTRODUCTION.

It is a well known fact that in substituted aromatic compounds the firmness with which atoms of halogen are attached to the benzol ring is diminished by the presence of nitro groups in certain positions, so that these atoms can be replaced by reagents, which would have no effect on them if the nitro groups had been absent. It has also been shown that certain other negative radicals exert a similar loosening effect: these are the two oxygen atoms in substituted quinones — chloranil and bromanil are very reactive bodies — the hydroxyl groups in phenols,\* and especially in substituted resorcline,† and also probably carboxyl.‡ The object of the research described in the present paper was to determine whether such a loosening effect could be produced by less negative radicals, and for this purpose we have taken up the study of derivatives of benzol, in which the substituting radicals are halogens only, so that both the radicals removed and those which make the removal possible belong to this same class, and the latter are distinctly less negative than any of those enumerated above. The amount of work already done in this field is meagre. Balbiano § found that paradibrombenzol was converted into parabromphenetol, brombenzol, and a little benzol, when it was heated to 190° with sodic ethylate. The same substance with sodic methylate at 150° gave

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\* Armstrong and Harrow, Journ. Chem. Soc., 1886, p. 447.

† Jackson and Dunlap, These Proceedings, XXIX. 228.

‡ Rahlis, Ann. Chem., CXCVIII. 112.

§ Gazz. Chim., XI. 401.

according to Blau\* parabromphenol, parabromanisol, and a little hydroquinone dimethylether. Blau† also found that symmetrical tribrombenzol gave with sodic methyrate at 130° symmetrical dibromphenol and the corresponding anisol as principal products. These results indicate that the atoms of bromine in these di- and tribrombenzols exert some loosening effect, as monobrombenzol must be heated to 200° before it reacts with sodic methyrate;‡ but all these actions take place in sealed tubes, and even the maximum difference between their temperatures of reaction and that of monobrombenzol is not very great, only 70°. We decided therefore, in taking up this subject, to try to obtain reactions in open vessels, that is, under conditions which would have prevented all action with monobrombenzol, and to do this it was obvious that we must increase the number of the atoms of halogen which are to produce the loosening effect. We selected for our first experiment accordingly the tribromiodbenzol having the constitution Br.H.Br.I.Br.H, as in this compound we have iodine as the element to be removed, and this is usually less strongly attached to the ring than bromine or chlorine, and the three atoms of bromine which are to produce the loosening effect are in the most favorable positions for this purpose (two ortho and one para). Trichloriodbenzol would probably have been even better, because chlorine is more negative than bromine, but we preferred the bromine compound on account of the great difficulty of preparing the trichloraniline in quantity.

Upon trying a variety of reagents with the unsymmetrical tribromiodbenzol, we obtained negative results with all except two, sodic ethylate and sodic methyrate. These converted it into symmetrical tribrombenzol, melting point 119°, by replacing the iodine with hydrogen, the sodic ethylate acting to some extent even in the cold, more freely when the solution in alcohol and benzol was boiled under a return condenser, while the sodic methyrate did not act in the cold, and only to a limited extent boiling. The unsymmetrical tetrabrombenzol Br.H.Br.Br.Br.H, which differs from the preceding compound only in having an atom of bromine in place of the iodine, was also partially converted into symmetrical tribrombenzol by boiling with sodic ethylate, but there was much less action than with the iodine compound, the tetrabrombenzol undergoing about as much substitution when the solution was boiling, as was the case with the tribromiodbenzol in the cold. The tribromchlorbenzol Br.H.Br.Cl.Br.H, on the other

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\* *Monatsh. f. Chem.*, VII. 627.† *Ibid.*, 630.‡ *Ibid.*, 636.

hand, was entirely unaffected by a solution of sodic ethylate in open vessels. These experiments show that the presence of the three bromine atoms exercises a loosening effect similar to that exhibited by nitro groups, although much weaker in degree. They also furnish an additional case in which the stability of the aromatic compounds of the different halogens increases in the order iodine, bromine, chlorine. This is worth noting, because Körner \* states that the halogens are removed from dinitrohalogenbenzols (X 1, NO<sub>2</sub> 2, NO<sub>2</sub> 4) in exactly the reverse order; that is, chlorine most and iodine least easily.

We next turned our attention to the tetrabrombenzol melting at 174°–175° which has been proved by work done in this Laboratory to have the symmetrical constitution Br.Br.H.Br.Br.H, as in this substance only two of the bromine atoms are in the positions to the one to be removed (ortho and para) which had proved effective in the unsymmetrical compound. This, however, did not affect the result materially, as this tetrabrombenzol was converted into unsymmetrical tribrombenzol (Br 1, Br 2, Br 4) by the boiling solution of sodic ethylate to about the same extent as the unsymmetrical tetrabrombenzol. In separating the small quantity of tribrombenzol formed from the large amount of unaltered tetrabrombenzol we have obtained excellent results in both the cases just mentioned by exposing the mixture for a long time to the lowest temperature at which anything sublimes. The sublimate thus obtained, if not the pure tribrombenzol, could be converted into it by a single repetition of this rough fractional sublimation.

An arrangement of the bromine atoms entirely different from the effective ortho para positions is found in the symmetrical tribrombenzol Br.H.Br.H.Br.H, as here all the halogen atoms are in the meta position to each other, but, as has been already mentioned, Blau found that one of the atoms of bromine was removed by the action of sodic methylate at 130°. As our work just described has shown that sodic ethylate is more active than the methylate, we thought this might act even in open vessels, and on trying the experiment have found that sodic ethylate in boiling alcoholic solution removes from symmetrical tribrombenzol a portion of its bromine. The organic products of the partial reaction were oily, but, as the object of our experiment was to determine whether a reaction took place, and not what its products were, no attempt was made to examine them. This is not the only

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\* Gazz. Chim., 1874, p. 323, note.

case in which one of three radicals in the symmetrical position has been removed, as Lobry de Bruyn \* has converted symmetrical trinitrobenzol into dinitranisol or dinitrophenetol by the action of the sodic alcoholates in open vessels. The work of Blau and Lobry de Bruyn, therefore, establishes this as a general behavior of symmetrical compounds, and such replacements are the more remarkable, because a single negative radical has no effect upon one other in the meta position.

In the work with unsymmetrical tetrabrombenzol, mentioned above, it was only the fourth atom of bromine (in the diortho para position to the others) that was replaced by hydrogen, but in some work upon the corresponding dinitro compound  $C_6Br_4(NO_2)_2$ , done some years ago by W. D. Bancroft and one of us, this atom of bromine remained obstinately unattacked when other atoms of bromine were removed; † in the same way the reduction of tetrabromdinitrobenzol with tin and hydrochloric acid gave monobromphenylene diamine, ‡ so that in these cases the symmetrical atoms of bromine alone were removed, and the action was exactly the reverse of that obtained with tetrabrombenzol and sodic ethylate. This difference is explained by the facts that in the tetrabrombenzol the three atoms of bromine in the trimeta position are the loosening radicals, whereas in the tetrabromdinitrobenzol they are those which are loosened. In this connection we decided to try the action of sodic ethylate on tetrabromdinitrobenzol, as this experiment had not been included in the previous work of W. D. Bancroft and one of us, and we found that tetrabromdinitrobenzol ( $Br.NO_2.Br.NO_2.Br.Br$ ) was converted by the action of a cold solution of sodic ethylate into the tribromnitroresorcine diethylether melting at  $101^\circ$ , and first obtained by W. H. Warren and one of us § by the action of sodic ethylate on tribromtrinitrobenzol. This substance has the formula  $C_6Br_3NO_2(OC_2H_5)_2$ , and must have been formed in this case by the replacement of one nitro group and the fourth atom of bromine by ethoxy groups, just as it was formed from the tribromtrinitrobenzol by the replacement of two nitro radicals by ethoxyls. If the action with the tetrabrom body is analogous to that with the trinitro compound, there should be formed at the same time by a parallel reaction a substituted phloroglucine, in this case dinitrobromphloroglucine or its ethers;

\* Rec. d. Tr. Chim., IX. 208, XIII. 149.

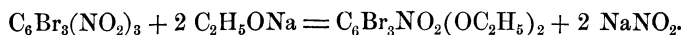
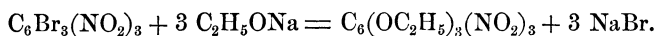
† These Proceedings, XXIV. 288. Sodium malonic ester gave the compound  $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$ ; reduction of this gave bromamidoxindol; aniline gave  $C_6Br(NO_2)_2(C_6H_5NH)_3$ .

‡ See the following paper.

§ These Proceedings, XXV. 183.

but although we have found indications that such a substance is formed, we have not succeeded in isolating it.

The principles governing the replacement of radicals attached to the benzol ring, which we have brought forward in this introduction, make it possible to explain the strange behavior of tribromtrinitrobenzol with sodic ethylate. This action consists in the two following reactions, which take place side by side.\*



In this substance we seem to have two zones of action, one consisting of the three symmetrically disposed bromine atoms, the other of the three nitro groups also symmetrically disposed, and the action in each molecule is confined to one of these zones, if it is carried on in the cold. In the first or bromine zone the atoms of bromine are submitted to two loosening influences: (*a*) that of the three nitro groups in the diortho and para positions to each bromine atom, and (*b*) that of the trimeta bromine atoms on each other. In the second or nitro zone also we have two loosening influences: (*c*) that of the three bromine atoms diortho and para to each nitro group, and (*d*) the loosening effect of the three symmetrical nitro groups on each other. Of these loosening influences (*a*) is by far the strongest, and (*b*) the weakest; it seems therefore that the combined effect of (*c*) and (*d*), of intermediate strength, is about equal to that of (*a*) and (*b*) together; consequently each of these zones of action lies about equally open to the attack of the sodic ethylate, and the two reactions take place simultaneously. When the solvent is alcohol alone, they run to about the same extent. If the repellent action of the three symmetrical nitro groups (*d*) is removed, that is, if tribromdinitrobenzol is used instead of the trinitro body, the nitro groups should be much less loosened than the bromine atoms, and as a matter of fact there has been observed in this case no tendency to remove the nitro groups, the action being confined to the bromine zone, causing the formation of  $\text{C}_6\text{Br}(\text{OC}_2\text{H}_5)_2(\text{NO}_2)_2\text{H}$ , or  $\text{C}_6\text{H}(\text{OC}_2\text{H}_5)_2(\text{NO}_2)_2\text{H}$ .

The work described in this paper has furnished us with three additional cases, in which atoms of halogens have been replaced by hydro-

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\* These Proceedings, XXVII. 283. Tetrabromdinitrobenzol acts in the same way, as just stated, but for the sake of simplicity of expression the explanation has been confined to the trinitro body, although it applies equally well to the tetrabrom compound.

gen under the action of sodic ethylate, but even with these we do not feel that enough facts are known to make it possible to deduce a general rule in regard to the conditions, which produce this curious reaction. The collection of such facts will be continued in this Laboratory.

We also tried the action of fuming nitric acid on unsymmetrical tribromiodbenzol, and found that iodine was set free, and the organic product was the tribromdinitrobenzol melting at  $192^{\circ}$ , and having the constitution  $\text{Br}.\text{NO}_2.\text{Br}.\text{NO}_2.\text{Br}.\text{H}$ .

A few statistics which we have collected about the removal of radicals from substituted benzols may be given here. By far the greater number of such removals are those in which a negative radical stands in the ortho position to the radical removed. Of these we have counted over sixty cases, in only nine of which the negative radical is a halogen. Of the cases of removal, where there is no negative radical in the ortho position, we have found four in which a negative radical is in the para position to the radical removed; these are  $\text{C}_6\text{H}_4\text{Br}_2$ ,  $\text{C}_6\text{H}_4\text{ClNO}_2$ ,  $\text{C}_6\text{H}_4\text{BrNO}_2$ , and  $\text{C}_6\text{H}_4(\text{NO}_2)_2$ ; and to these perhaps should be added five of the nine cases mentioned above, in which the ortho radical is a halogen, as in all of these there is a nitro group in the para position to the radical removed.\* In no case is a radical removed which is only in the meta position to a single negative radical; † but if there are two negative radicals in meta positions to the radical attached (symmetrical tri-compound), there are two cases in which substitution has been observed,  $\text{C}_6\text{H}_3\text{Br}_3$  and  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ .

#### EXPERIMENTAL PART.

##### *Behavior of Tribromiodbenzol.*

The tribromiodbenzol (I 1, Br 2, Br 4, Br 6) was made from symmetrical tribromaniline by replacing the amido group by an atom of iodine. Silberstein, ‡ who discovered this substance, made it from the nitrate of diazotribrombenzol. We have preferred to use the sulphate, and, as our method seemed to give a better result than Silberstein's

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\* In the other cases where a radical was removed, which was ortho only to halogens, these halogens were in the diortho position, and therefore probably were sufficient to cause the removal.

† The conversions of meta and para nitranisol into the corresponding nitranilines were not counted, because they took place at such a high temperature,  $200^{\circ}$ ; but perhaps they should be added to the list given above.

‡ Journ. Prakt. Chem., [2.], XXVII. 119.

to judge from his statement, we give it in detail. Ten grams of symmetrical tribromaniline were mixed with moderately dilute sulphuric acid in such proportion that there was one molecule of the acid to each molecule of the tribromaniline; the calculated amount of solid sodic nitrite was then added in small quantities at a time, shaking the loosely corked flask after each addition until the red fumes were absorbed. The mixture after standing over night was filtered, and then treated with hydriodic acid till there was no further action. The slightly brown precipitate was washed with water, and purified by crystallization from a mixture of benzol and alcohol, when it showed a melting point of  $104^{\circ}$ . Silberstein gives  $103^{\circ}.5$ . For greater safety it was analyzed, with the following result.

0.3374 gram of the substance gave 0.6119 gram of a mixture of argentic bromide and iodide.

	Calculated for $C_6H_2Br_3I$ .	Found.
Iodine and Bromine	83.24	83.32

We find the solubilities of the substance the same as those given by Silberstein, but we do not agree with him when he says it sublimes easily, as we have found that it sublimes much less easily than symmetrical tribrombenzol.

To study the action of sodic ethylate on tribromiodbenzol, 6 grams of it were dissolved in anhydrous benzol, and mixed with 40 c.c. of an alcoholic solution of sodic ethylate, containing 2 grams of sodium, that is, more than enough to remove all the halogen atoms present. The mixture was then heated on the steam bath under a return condenser for one hour, when the liquid had taken on a dark color, and a brownish precipitate had appeared; the liquid was now evaporated, and the residue treated for half an hour with a large quantity of water, filtered, and washed, when it weighed 4.1 grams. Upon subliming this residue, 2 grams of sublimate were obtained in small white needles which melted at  $119^{\circ}$ – $120^{\circ}$ , the melting point of symmetrical tribrombenzol. An analysis of the sublimate gave the following result.

0.2612 gram of the substance gave by the method of Carius 0.4695 gram of argentic bromide.

	Calculated for $C_6H_3Br_3$ .	Found.
Bromine	76.18	76.51

There can be no doubt, therefore, that the substance is tribrombenzol, formed by the replacement of the atom of iodine in the tribrom-

iodbenzol by hydrogen. The residue which did not sublime was a brownish yellow powder, containing many black specks. It did not melt at  $300^{\circ}$ , but melted with blackening when held over the free flame. It was not completely soluble in any of the common solvents, and all our efforts to obtain from it a body fit for analysis have proved fruitless.

The experiment was next repeated under the same conditions, except that the mixture was not heated, but allowed to stand three days at the ordinary temperature. At the end of this time it had turned dark brown, in fact a pale brown color appeared almost as soon as the materials were mixed; the solvents were then allowed to evaporate spontaneously, and the residue treated with water as in the previous experiment, when the aqueous filtrate gave a strong test with starch paste and chlorine water for iodine. The residue insoluble in water was sublimed at a very gentle heat, and crystals of symmetrical tribrombenzol were obtained recognized by their melting point,  $119^{\circ}$ – $120^{\circ}$ . The residue, which did not sublime at this gentle heat, was crystalline and of a reddish white color, very different from the amorphous brown product obtained under the same conditions from the action of hot sodic ethylate. This crystalline residue after three recrystallizations from a mixture of benzol and alcohol showed the melting point  $104^{\circ}$ , and was therefore unaltered tribromiodbenzol. It seems, therefore, that cold sodic ethylate behaves like hot, but the action is less complete. An alcoholic solution of sodic hydrate, after being warmed for ten minutes with a solution of tribromiodbenzol in benzol, converted it into tribrombenzol with elimination of iodine. This, therefore, acted in the same way as the hot solution of sodic ethylate, but the yield seemed to be larger, and the residue from the sublimation was lighter in color (yellow) and free from black specks. It did not, however, prove to be more manageable than that previously obtained. These differences may be due to the shorter heating, ten minutes in this case instead of one hour when the ethylate was used. Several attempts were made to detect the aldehyd, which it seemed probable was formed as the secondary product in the replacement of the iodine by hydrogen, but these led to no definite result.

Sodic methylate when boiled with a benzol solution of tribromiodbenzol for over an hour gives a result similar to that obtained from cold sodic ethylate; that is, tribrombenzol was formed, but there was a large amount of undecomposed tribromiodbenzol. The two substances were separated by careful sublimation, and recognized by their melting points. Cold sodic methylate, on the other hand, gave no

action even after standing three days. This was proved by testing the aqueous washings for halogens with negative results, and recovering essentially all of the tribromiodbenzol used.

The following reagents had no effect on the tribromiodbenzol: sodic phenylate in alcoholic solution boiling, sodic hydrate in aqueous solution boiling, sodic carbonate in aqueous solution boiling, zincic oxide and water in a sealed tube at  $200^{\circ}$  for twelve hours, argentic acetate in aqueous solution boiling, aniline boiling, tin and hydrochloric acid, sodium malonic ester both cold and hot. The proof that no action had taken place in these experiments was obtained either by the recovery of the unaltered tribromiodbenzol, or by tests for a salt of the halogens which gave negative results. In most cases both methods of proof were applied.

To determine whether the removal of the iodine was due to the loosening effect of the three atoms of bromine or to the slight attraction of iodine alone for carbon, iodbenzol was treated with sodic ethylate under the same conditions which had produced an action on the tribromiodbenzol; but after heating the mixture for an hour and a half no test for sodic iodide could be obtained, showing that there had been no action.

*Action of Fuming Nitric Acid on Tribromiodbenzol.*

When tribromiodbenzol was treated with fuming nitric acid, it lost its white crystalline appearance even in the cold, and became converted into a yellow powder. If the mixture was allowed to stand at ordinary temperatures over night, and then water added to it, iodine appeared both in scales and in the form of vapor, as a great amount of heat was given off. The identity of the iodine was also established by the smell and the violet color of its solution in carbonic disulphide. If now the insoluble portion was washed with cold alcohol until free from iodine, and then recrystallized several times from a mixture of benzol and alcohol, it showed the constant melting point  $191^{\circ}$ , which indicated that the substance was tribromdinitrobenzol, and this was confirmed by the following analysis.

0.3375 gram of the substance gave by the method of Carius 0.4740 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_2$ .	Found.
Bromine	59.26	59.78

The somewhat high result may be due to a trace of a substance containing iodine. If the mixture of tribromiodbenzol and fuming nitric acid was boiled, the organic product was the same, but no free iodine was obtained.

*Behavior of Unsymmetrical Tetrabrombenzol melting at 98°.*

The action of sodic ethylate on this substance was selected for study, because that reagent had given the best results in the work on tribromiodbenzol just described. To prepare the unsymmetrical tetrabrombenzol, 20 grams of tribromaniline were dissolved in 180 c.c. of hot glacial acetic acid, about 80 c.c., that is a considerable excess, of a distilled solution of hydrobromic acid (boiling point 125°) added, and, disregarding any precipitate formed, the mixture treated with sodic nitrite in the proportion of a molecule and a half or two molecules to each molecule of the tribromaniline. For this purpose the finely powdered nitrite was slowly sifted with vigorous stirring into the solution, which had previously been cooled so that it felt barely warm to the hand. The white crystals which were suspended in it gradually changed into a dirty brown solid, much of which dissolved even in the cold. The mixture was then heated for two or three hours on the water bath; the solid matter at first went into solution, but later the tetrabrombenzol, as it formed, separated, principally in long white needles, or sometimes in part as a semiliquid brown mass. The needles were separated mechanically, and were usually found to be pure. The semiliquid portion solidified in a short time, and was purified by dissolving it in a little hot benzol, and pouring this solution into alcohol. The tetrabrombenzol precipitated in this way had a slight reddish color, while the mother liquor was of a dark claret-red. The precipitate was easily obtained white by one or two recrystallizations from a large volume of alcohol, to which it was well to add a little benzol. In this way 20 grams of the tribromaniline gave 22 grams of tetrabrombenzol, instead of the 23.88 grams required by the theory, a yield of 92 per cent.

Eight grams of the tetrabrombenzol were mixed with an alcoholic solution of sodic ethylate, made from 2 grams of sodium and 50 c.c. of absolute alcohol, and a little benzol to assist the solution of the tetrabrombenzol. The mixture was heated to boiling under a reverse condenser for two days, when it had taken on a blackish green color; it was then evaporated to dryness, and washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was sublimed at the lowest possible temperature, when a

small amount of white needles was obtained, which melted at  $119^{\circ}$ , the melting point of symmetrical tribrombenzol. The residue which had not sublimed at the very low temperature used made up the principal bulk of the product, and was chiefly unaltered tetrabrombenzol. This method of fractional sublimation has also yielded us excellent results in another similar case, which will be described later in this paper. The sodic ethylate therefore acts on the tetrabrombenzol in the same way that it does on the tribromiodbenzol, replacing by hydrogen the bromine atom occupying the same position as the atom of iodine, but the action takes place with more difficulty, and is less complete.

*Behavior of Unsymmetrical Tribromchlorbenzol.*

The tribromchlorbenzol was prepared by a method similar to that used for the tetrabrombenzol. Upon adding the hydrochloric acid to the solution of tribromaniline in glacial acetic acid a precipitate of the chloride was formed, but this went into solution as the amido was converted into the diazo compound. Twenty grams of tribromaniline yielded 15 grams of tribromchlorbenzol melting at  $82^{\circ}$ . Two grams of this substance were heated for four hours with an alcoholic solution of sodic ethylate, prepared from half a gram of metallic sodium; when upon evaporation to dryness and washing with water only a very faint test for halogens could be obtained from the wash water, and the residue, which consisted of unaltered tribromchlorbenzol, weighed nearly 2 grams. A similar experiment with the tetrabrombenzol, in which the mixture was boiled for only three hours, gave a strong test for sodic bromide and a small amount of tribrombenzol. The chlor-tribrombenzol, therefore, if affected at all by sodic ethylate, is much less susceptible to its action than either the corresponding iod or brom compound.

*Behavior of Symmetrical Tetrabrombenzol.*

Tetrabrombenzol, melting at  $174^{\circ}$ – $175^{\circ}$ , which has been proved by work done in this Laboratory to have the symmetrical constitution (1, 2, 4, 5), was boiled for over twelve hours with an alcoholic solution of sodic ethylate; the brown liquid thus obtained, with some long rather dark colored crystals, which were deposited as it cooled, was evaporated to dryness, and the residue washed with water. The wash waters gave a good test for sodic bromide. The residue insoluble in water was then extracted, with a mixture of alcohol and benzol, filtered to remove a brown insoluble substance, and the filtrate concen-

trated, when it deposited crystals which melted at  $174^{\circ}$ – $175^{\circ}$ , and were therefore the unaltered tetrabrombenzol. The mother liquor was evaporated to dryness, and cautiously sublimed at as low a temperature as possible; the crude sublimate melted at  $42^{\circ}$ – $43^{\circ}$ , and upon resubliming it with the same care its melting point rose to  $44^{\circ}$ , the melting point of unsymmetrical tribrombenzol (1, 2, 4), which must be formed if one of the atoms of bromine is removed from this tetrabrombenzol. Only a small portion of the substance, however, reacts with the sodic ethylate, by far the greater part remaining unaltered.

*Experiment with Symmetrical Tribrombenzol.*

Blau\* states that tribrombenzol is converted by sodic methylate into symmetrical dibromphenol, when the substances are heated together in methyl alcohol solution for two to three days at  $120^{\circ}$ – $130^{\circ}$ . We accordingly tried an experiment to see whether sodic ethylate would have a similar action in open vessels, as we had used this reagent in the preceding work. Ten grams of tribrombenzol were boiled with a solution of the necessary amount of sodic ethylate in about 200 c.c. of alcohol for somewhat more than seventy hours; the aqueous wash waters from the product gave a good test for sodic bromide, and in addition to a large amount of unaltered tribrombenzol we obtained a very little of an oil, probably the dibromphenol ethylether, which is a liquid. As this result, which it will be observed confirms Blau, had given us all the information about the reaction which we wished, we did not pursue the work further.

Hexabrombenzol gave when boiled with sodic ethylate a good test for sodic bromide. The organic product was an oil, and a great deal of unaltered hexabrombenzol was recovered. Hexachlorbenzol gave a similar result.

*Action of Sodic Ethylate on Tetrabromdinitrobenzol.*

In the experiments described in this paper the fourth atom of bromine was removed from tetrabrombenzol by sodic ethylate, while in the work by W. D. Bancroft and one of us † upon the tetrabromdinitrobenzol, this fourth atom of bromine was not removed by aniline or sodium malonic ester. It seemed of interest therefore to try the tetrabromdinitrobenzol with sodic ethylate, and see whether it behaved like the tetrabrombenzol with this reagent or in the same way

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\* Monatsh. f. Chem., VII. 630.

† These Proceedings, XXIV. 288.

that it had behaved with the other reagents mentioned above. For this purpose 10 grams of tetrabromdinitrobenzol were dissolved in benzol, and treated with an alcoholic solution of the sodic ethylate made from 2 grams of sodium. The solution became claret-colored as soon as the sodic ethylate was added, but this color changed later to a reddish brown. There was no perceptible evolution of heat. The mixture was allowed to stand at ordinary temperatures for two days, after which it was evaporated spontaneously. The residue, after being washed with water, was recrystallized from alcohol until it showed the constant melting point  $100^{\circ}$  to  $101^{\circ}$ . This showed that it must be the tribromnitroresorcine diethylether made by Warren and one of us \* from tribromtrinitrobenzol. This substance must have been formed by the replacement of one nitro group, and the fourth atom of bromine by two ethoxy radicals. To confirm this the wash waters of the original product were tested for a bromide and a nitrite, and good results obtained in both cases. If in this case the reaction has run as with tribromtrinitrobenzol,† which we should infer from the isolation of tribromnitroresorcine diethylether, the secondary product should be bromdinitrophloroglucine, or its ethers. As a matter of fact, an oil having the properties of a phenol was obtained by acidifying the aqueous wash waters from the first product of the reaction, but all our attempts to bring it into a form fit for analysis have failed, and we have been prevented from continuing work on this substance by the departure of one of us from Cambridge.

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\* These Proceedings, XXV. 183.

† Ibid., XXVII. 283.